

APPARATUS AND METHOD FOR PREVENTING
THE FORMATION OF METAL TARNISH

FIELD OF INVENTION

The present invention relates to an apparatus and a method for preventing the formation
5 of tarnish on silver, copper, or brass objects. In particular, the present invention relates to a
construction of such apparatus using carbonaceous adsorbents to significantly reduce or eliminate
tarnishing agents from contacting of such objects.

BACKGROUND OF THE INVENTION

Tarnish is a term which describes the visual change in the lustrous surface of a metal after
it has reacted with various atmospheric components. Most frequently, tarnish is associated with
the discolorization of objects made of silver; silver alloys, in which silver is the predominant
component; copper; or brass, which is an alloy of copper and zinc. The chemical process which
causes tarnish is the corrosion of the metal surface through an oxidative process. However, the
primary route of oxidation, in many instances, can be caused by materials other than oxygen. It
is well known that silver and silver alloys tend to tarnish in the gaseous atmospheres containing
hydrogen sulfide or other sulfide compounds, even in small concentrations, particularly in the
simultaneous presence of ammonia, resulting in a dull or black finish. Copper reacts with
hydrogen sulfide in a similar fashion as silver because both elements have the same outermost
electron shell configuration according to the Periodic Table. However, copper is more reactive
20 than silver and after the initial tarnishing by hydrogen sulfide to produce a red or dark brown
surface, it can further react with carbon dioxide in the atmosphere to produce a green patina
which has been associated with older copper structures such as the Statue of Liberty.

The sources and concentrations of hydrogen sulfide in the atmosphere and indoor air are varied. Man-made sources of hydrogen sulfide include industrial emissions from the burning of fossil fuels, natural gas, chemical plants, poorly ventilated sewage lines, sewage treatment facilities, and farms. Natural sources include geothermal emissions, anaerobic bacterial processes, and salt water bodies. In the indoor environment, gaseous by-products from human digestive processes are a major source. It is, therefore, difficult to place a value on what might be considered an average or typical range for hydrogen sulfide concentrations in the atmosphere or indoor environment. The U.S. Environmental Protection Agency ("USEPA") has estimated that the average concentration for hydrogen sulfide in the atmosphere is 0.1 to 0.3 parts per billion ("ppb") (see USEPA report number EPA/600/8-86/026F, *Health Assessment Document for Hydrogen Sulfide*, January 1993). It should be clearly noted that this is an average concentration and peak levels may be higher by several hundred fold as is evident in the USEPA report.

The control of hydrogen sulfide also has long been a concern in the area of prevention of corrosion, due to low levels of hydrogen sulfide, of silver and copper electronic contacts in sensitive electronic equipment. The tarnishing and corrosion of silver and copper contacts can result in the premature failure of electronic equipment.

Sulfide films on silver or copper objects can be removed from their surfaces by chemical treatment or polishing. The formation of sulfide films can be prevented by forming on the objects a film of another stable metal, such as rhodium, or of oxide of aluminum, beryllium, technetium, or zirconium. However, all of these methods have disadvantages. Chemical treatment and polishing gradually remove part of the original metal. Accidental scratches in the

film of stable metal or oxides expose the fresh silver or copper surface to attack by hydrogen sulfide.

Therefore, it is an object of the present invention to provide an apparatus and a method for preventing or inhibiting the formation of tarnish on objects made of silver, copper, or mixtures thereof. It is a further object of the present invention to provide regenerable activated carbon articles forming interior surfaces or linings of such an apparatus for surrounding such objects. These and other objects of the present invention will become apparent upon a perusal of the present disclosure.

SUMMARY OF THE INVENTION

In general, the present invention provides an apparatus comprising flexible adsorbent articles for enclosing objects made of silver, copper, or mixtures thereof significantly reduce or eliminate tarnishing agents from therein and to prevent or inhibit the formation of tarnish on such objects. The flexible articles comprise one or more adsorbents, such as activated carbon, natural or synthetic zeolite, activated alumina, or silica gel. These adsorbents may be incorporated in flexible fibrous matrixes which are capable of being formed into a variety of shapes.

One particularly suitable adsorbent is activated carbon cloth ("ACC"), which has a faster adsorption kinetics than the common forms of activated carbon, is manufactured in thermal processes from woven or non-woven natural, man-made, or synthetic fibers and which possesses a high surface area for adsorption. The raw material fiber is preferably chosen for its desirable properties. Flexible ACC removably attaches to interior surfaces or linings so that the ACC substantially surrounds the metal objects to be protected.

Commonly encountered tarnishing agents include hydrogen sulfide, sulfur oxides, carbonyl sulfide, carbon disulfide, nitrogen oxides, ozone, halogen gases, ammonia, ammonium salts, and mixtures thereof. The reaction of many of these tarnishing agents on silver, copper, and mixtures thereof may be accelerated in the presence of water vapor. When the adsorptive capacity of the ACC has been exhausted, it may be removed from the apparatus and regenerated for reuse. Regeneration may be achieved by, for example, washing the ACC and heating it to a temperature less than about 350 °C. The regenerated ACC may then be reinserted or reattached to the apparatus to provide continued protection of the metal objects.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a perspective drawing of one embodiment of the present invention showing a storage box with ACC removably attached to the interior surfaces of the box.

Figure 1a shows ACC laminated with an adhesive between layers of protective fabric or cloth.

Figure 2 is a perspective drawing of another embodiment of the present invention showing a resealable bag, the interior surface of which is lined with ACC.

Figure 3 shows corrosimetry data of silver and copper, unprotected and protected by an apparatus of the present invention, in an atmosphere containing 1,000 ppb (by volume) of hydrogen sulfide.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention uses adsorbents capable of removing tarnishing agents from atmospheric air. Adsorbents having high adsorptive capacity for hydrogen sulfide, sulfur oxides, carbonyl sulfide, carbon disulfide, nitrogen oxides, ozone, halogen gases, ammonia and ammonium salts includes activated carbon, natural and synthetic zeolite, activated alumina and 5 silica gel. The presently preferred adsorbent is ACC which generally is activated carbon in the form of woven, non-woven, or knitted fabric, cloth, or sheet.

ACC may be suitably manufactured, for example, from cotton, cellulose, cellulose derivatives, wool, polyester, rayon, nylon, polyethylene, polypropylene, polytetrafluoroethylene, polyamide, polyacrylonitrile, other polymeric materials or combinations thereof. Other suitable 10 man-made raw materials are pitches derived from coal tar or petroleum residues. Any of these materials may be formed into micron-sized fibers or filaments, several of which may be bundled together to produce a yarn. The yarn may be woven or knitted together to form a fabric or cloth. Alternatively, sections of the micron-sized fibers or filaments may be compressed or attached 15 together to form a felt, mat or sheet. Rayon fiber produced by the viscose process is a particularly suitable raw material for the production of ACC.

The woven, non-woven, or knitted fabric, felt, mat or sheet of the chosen fiber is carbonized thermally at a temperature less than about 500 °C in an atmosphere of carbon dioxide, air, nitrogen or a combination thereof. The carbonized fiber may be impregnated with one or more halides of zinc, aluminum, magnesium, calcium, iron and ammonium; or phosphoric acid 20 and dried prior to thermal carbonization because these chemicals have been known to result in a higher yield of the carbonized material. The preferred halides are chlorides; but fluorides, bromides, or iodides also may be used. The total amount of impregnants will depend upon the

raw material used, but it typically amounts to less than 20 percent by weight of the raw material.

Subsequent to the thermal carbonization step, the carbonized material is further treated thermally at a temperature greater than about 700 $^{\circ}\text{C}$ preferably in an inert gas atmosphere such as nitrogen, helium, argon, krypton, xenon, or a combination thereof. However, it may be

5 desirable in some instances to carry out the thermal treatment in an atmosphere comprising steam or carbon dioxide to impart desirable properties to the ACC. For example, this type of atmosphere may be desirable to provide a lower-density ACC. If the fabric is impregnated with metal halides or phosphoric acid prior to carbonization, the thermally treated material may be desirably washed with a solvent such as water and dried to remove the impregnants. The
10 thermally treated carbonaceous woven, non-woven, or knitted fabric, felt, mat, or sheet possesses a high adsorptive rate and capacity for hydrogen sulfide, sulfur oxides, carbonyl sulfide, carbon disulfide, nitrogen oxides, ozone, halogen gases, ammonia, ammonium salts, and mixtures thereof. The ACC may be desirably impregnated with compounds which enhance its adsorptive capacity for these contaminants.

15 In a preferred embodiment of the present invention, shown in Figure 1, ACC 10 was removably attached to interior surfaces 12, 13 and 14 of a storage case 21. The surfaces of the ACC facing the interior of the storage case were covered with a decorative or protective fabric or cloth 22. Alternatively, the ACC may be pressure laminated with an adhesive 24 between two layers of protective fabric or cloth 26 and 27, shown in Figure 1a, before being removably
20 attached to the interior surfaces of the storage case 21. Adhesive 24 and protective fabric or cloth 26 and 27 used for the lamination process are preferably chosen such that the laminated ACC piece may be regenerated by washing with a solvent such as water and heating up to 350 $^{\circ}\text{C}$ after

its adsorptive capacity has been exhausted. The ACC-lined storage case 21 of the first preferred embodiment of the present invention provide protection against atmospheric tarnish agents to valuable objects such as jewelry, silverware, coins, brass musical instruments, and the like.

In another preferred embodiment of the present invention, shown in Figure 2, a resealable bag 41 was lined with ACC 42 and covered with fabric or cloth 43. Resealable bag 41 may have a closure means 50, preferably constructed of Velcro®. Alternatively, the ACC 42 could be laminated between two layers of protective fabric or cloth prior to being affixed inside the bag. The resealable bag may also be constructed to accommodate washing (and heating) for reuse when the adsorptive capacity of the ACC has been exhausted, in the manner described above.

10 **TESTING OF A STORAGE CASE OF THE PRESENT INVENTION**

A commercial jewelry box (purchased from K-Mart Corporation) fitted with FM1-250 ACC (available from Calgon Carbon Corporation, Pittsburgh, Pennsylvania) in the interior thereof, including the ring cushions and around the closure surface, was tested for its ability to prevent the tarnish of silver and copper. A gap of approximately 1/16 inch remained between the lid and the box sealing surfaces when the box was closed. The jewelry box was placed in a test chamber consisting of a plastic desiccator which was continuously purged with a stream of high humidity air (80% relative humidity ("RH")) containing 1000 ppb (by volume) of hydrogen sulfide. Silver and copper articles (sterling jewelry and coins) were placed inside and outside of the modified jewelry box in the test chamber along with commercially available corrosimeter probes constructed of silver and copper. Clean copper coins placed outside of the modified jewelry box showed visible tarnish in a period of 1 hour (accelerated 0.5 years). Silver jewelry

showed visible tarnish in 6 hours (accelerated 2.3 years) in the same environment. Test results are shown in Figure 3. These results are consistent with the relative rates of silver and copper tarnish based on chemical reactivity, copper being a more reactive metal than silver. After extended periods of time, the tarnish of the silver jewelry became very pronounced with
5 blackening of the object. Lower grade silver articles would be expected to exhibit tarnish in a shorter period of time.

The level of hydrogen sulfide used in the experiments was far in excess of the normal average encountered in the atmosphere (0.1 to 0.3 ppb). This was done in order to accelerate the tarnishing process from what is normally months and years to days. High RH also accelerates the
10 tarnishing process. The factor used to calculate the time accelerated corrosion results was 3333 (i.e., 1000/0.3) since it has been known that corrosion, and therefore, tarnishing of silver, is linear with concentration (J.P. Franey and G.W. Kammlott, *Corrosion Science*, Vol. 25, p. 133 (July 1985)). It is important to note that the average hydrogen sulfide concentrations reported by the USEPA do not take into account peak levels which may be several hundreds of times higher.

In the unprotected environment, copper and silver exhibited high corrosion rates as were measured in corrosimeter probes. The corrosion rates were determined with a Rohrback Cosasco Model CK-3 Corrosimeter (Rohrback Cosasco Systems, Inc., Santa Fe Springs, California). These corrosion rates are much higher than the most severe classification (GX) for corrosion as is adopted by the Instrument Society of America, which corresponds to a corrosion rate of greater
20 than 2000 Angstrom per accelerated month for copper.

Silver jewelry and copper coin protected by the ACC-lined jewelry box exhibited markedly decreased tarnish within the same corrosive environment. The silver jewelry did not

exhibit any visible tarnish throughout the experiment (accelerated 35 years). The copper coin showed slight visible tarnish after an accelerated 15 years. The corrosimeter results indicated a 90% reduction of the corrosiveness, as is exhibited by the relative corrosion rates of the corrosimeter probes located inside and outside of the jewelry box, of the environment protected 5 by the ACC even after an accelerated 15 years. Therefore, it is assumed that silver and copper stored within an apparatus of the present invention would be protected from tarnish for an extended period of time.

It is expected that the protection by an apparatus of the present invention would also extend to items fabricated from brass. It is estimated that under average atmospheric conditions,

0 the protection period would be 15 years. The actual amount of time that the articles would be protected from tarnish would depend on the concentration of corrosive gases in the home, relative humidity, and the amount of time during which the jewelry box remains open. Of course, the degree of tarnish would also depend on the amount of time during which the articles are outside of the box and the atmosphere to which these articles are exposed.

15 While the foregoing has described the preferred embodiments and modes of operation of the present invention, it should be appreciated that numerous variations, changes, and equivalents may be made to these embodiments and modes of operation without departing from the scope of the present invention as is defined by the following claims.